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Abstract

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Preparation of Halogen Anhydrides of α,β-Alkenylphosphoric Acids

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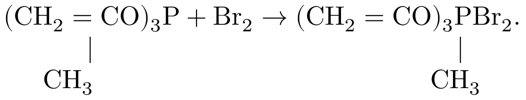
In the present work, the reaction of vinyl and substituted vinyl esters of phosphorous acid with halogens and phosphorus pentachloride has been studied. As is known, trialkyl phosphites react with halogens and other halogenating agents according to the scheme of the Arbuzov rearrangement, with formation of halogen anhydrides of phosphoric acid (^{1}):

$$(RO)_3P + X_2 \rightarrow [(RO)_3PX_2] \rightarrow (RO)_2P(O)X + RX.$$

Triaryl phosphites, on interaction with halogens and also with phosphorus pentachloride, form stable addition products of the phosphonium type–$(ArO)_3PX_2$, which do not undergo the Arbuzov rearrangement (^{2}). It could be assumed that the halogen addition products to alkenyl phosphites, in terms of stability, would occupy an intermediate position between compounds of this type for alkyl and aryl phosphites.

When bromine was added to a benzene solution of triisopropenyl phosphite or diisopropenyl phenyl phosphite, formation of a white crystalline precipitate was observed. Isolation and investigation of the substances obtained showed that they are quasiphosphonium compounds. The halogen adds primarily to the phosphorus atom, without affecting the double carbon-carbon bond of the alkenyl radical of the phosphite:



$$(CH_2 = \underset{\displaystyle CH_3}{\underset{|}{C}}O)_3P + Br_2 \rightarrow (CH_2 = \underset{\displaystyle CH_3}{\underset{|}{C}}O)_3PBr_2.$$

The quasiphosphonium compounds obtained in this way are insoluble in ether, benzene, and petroleum ether, and are stable at room temperature. However, if they are heated, they first melt and then decompose. Further study of the decomposition showed that, in this process, bromine anhydrides of alkenylphosphoric acids are formed in high yields.

Thus, the quasiphosphonium compound obtained from diisopropenyl phenyl phosphite and bromine melts at 38-40° on heating, and at 50° and above begins to decompose. After heating in benzene solution (70-80°, 1 hour) the quasiphosphonium compound obtained from diisopropenyl phenyl phosphite and bromine, isopropenylphenylphosphoric bromine anhydride was isolated in 90% yield. Phosphites containing both alkyl and alkenyl radicals should naturally not give quasiphosphonium compounds stable at room temperature.

Indeed, when bromine was added to a benzene solution of ethyl diisopropenyl phosphite, butyl diisopropenyl phosphite, and butyl divinyl phosphite, formation of crystalline quasiphosphonium compounds was not observed. The intermediately formed products of bromine addition to the named alkenylalkyl phosphites undergo a normal Arbuzov rearrangement, giving, in 80–90% yield, bromine anhydrides of divinyl- and diisopropenylphosphoric acids:

$$(\mathrm{RO})\mathrm{P}(\mathrm{OCH}=\mathrm{CH}_2)_2+\mathrm{Br}_2\rightarrow(\mathrm{CH}_2=\mathrm{CHO})_2\mathrm{P(O)Br}+\mathrm{RBr}.$$

Bromoanhydrides of dialkenylphosphoric acids are transparent liquids; on storage they darken rapidly, and on redistillation they undergo noticeable decomposition.

Chloroanhydrides of α,β-alkenylphosphoric acids were obtained by the reaction of vinyl phosphites with phosphorus pentachloride. The following were used in the reaction: diisopropenyl phenyl phosphite, butyl diisopropenyl phosphite, diethyl isopropenyl phosphite, butyl divinyl phosphite, and dibutyl vinyl phosphite. The reaction of alkenyl phosphites with phosphorus pentachloride was carried out in carbon tetrachloride solution with cooling of the reaction mixture to −10–0°. In the case of diisopropenyl phenyl phosphite, formation of a white crystalline compound was observed. To complete the reaction, the reaction mixture was heated for one hour at 70–80°. Taking butyl divinyl phosphite as an example, the reaction may be represented by the following scheme:

$$(\mathrm{C}_4\mathrm{H}_9\mathrm{O})\mathrm{P}(\mathrm{OCH}=\mathrm{CH}_2)_2+\mathrm{PCl}_5\rightarrow$$

$$\rightarrow(\mathrm{CH}_2=\mathrm{CHO})_2\mathrm{P(O)Cl}+\mathrm{C}_4\mathrm{H}_9\mathrm{Cl}+\mathrm{PCl}_3.$$

The chloroanhydrides of α,β-alkenylphosphoric acids were isolated in yields of 60 –80%. They are stored well for a long time and, on distillation, are considerably more stable than the corresponding bromoanhydrides.

Thus, under the action of bromine and phosphorus pentachloride on vinyl and substituted vinyl esters of phosphorous acid, the corresponding haloanhydrides of phosphoric acid are isolated in all cases (see Table 1). At the same time, if the phosphite contains alkyl and alkenyl radicals, cleavage of only the alkyl radical is observed, which corresponds to the general scheme of the Arbuzov rearrangement for alkyl alkenyl phosphites ([3]). If, however, the phosphite contains only α,β-alkenyl radicals or phenyl and alkenyl radicals, formation is observed of a crystalline quasiphosphonium compound stable at room temperature. A study of the mechanism of decomposition of the resulting quasiphosphonium compounds showed that in this case normal Arbuzov rear—

Table 1

Haloanhydrides of α,β-alkenylphosphoric acids

Haloanhydrides	Starting phosphites	Yield, %	b.p., °C/mm	n_D^{20}	d_4^{20}	MR_D, found	MR_D, calculated	Found, %, C	Found, %, H	Found, %, P	Calculated, %, C	Calculated, %, H	Calculated, %, P
$R'O(C_6H_5O)P(O)Br$	$(C_6H_5O)P(OR')_2$	90	128/0.5	1.5261	1.4748	57.68	57.94	39.14	3.68	10.19	39.02	3.64	11.18
$R'O_2P(O)Br$	$(C_4H_9O)P(OR')_2$	50	71.5–72/3	1.4700	1.3993	48.04	47.09	29.70	4.29	12.33	29.89	4.18	12.85
$R'O_2P(O)Br$	$(C_4H_9O)P(OR')_2$	80	75–76/2	1.4650	1.5263	38.58	37.95	22.41	2.97	13.68	22.56	2.84	14.55
$R'O(C_6H_5O)P(O)Cl$	$(C_6H_5O)P(OR')_2$	70	114–114.5/1	1.5040	1.2454	55.47	55.38	46.42	4.67	12.66	46.53	4.65	14.02
$R'O_2P(O)Cl$	$(n\text{-}C_4H_9O)P(OR')_2$	70	51–52/1	1.4425	1.1746	44.56	44.32	36.57	5.28	15.74	36.65	5.13	15.76
$R'O(C_2H_5O)P(O)Cl$	$(C_2H_5O)P(OR')_2$	60	68–70/4	1.4332	1.1861	40.46	40.41	32.61	5.39	17.07	32.53	5.34	16.78
$R'O_2P(O)Cl$	$(n\text{-}C_4H_9O)P(OR')_2$	80	60–61/12	1.4350	1.2442	35.35	35.32	28.40	3.74	18.37	28.34	3.59	18.38
$RO(n\text{-}C_4H_9O)P(O)Cl$	$(n\text{-}C_4H_9O)P(OR)_2$	80	60/3.5	1.4360	1.1529	45.02	45.03	—	—	15.73	—	—	15.26

$R = CH_2 = CH$; $R' = CH_2 = C(CH_3)$

grouping. Upon heating the quasiphosphonium compound obtained from diisopropenyl phenyl phosphite and bromine, instead of formation of the alkenyl bromide, methylacetylene was evolved in all cases. This direction of decomposition may be represented with the aid of a cyclic active complex:

$$\text{cyclic complex of } (C_6H_5O)PBr[OC(CH_3){=}CH_2] \text{ with an } HC{=}CH \text{ fragment}$$
$$\longrightarrow HC{\equiv}C{-}CH_3 + HBr + (C_6H_5O)(CH_2{=}CO)P(O)Br$$

Formation of methylacetylene was proved both by obtaining the characteristic bright-yellow precipitate of copper methylacetylide and by converting methylacetylene into 1,1,2,2-tetrabromopropane.

The halogen anhydrides of alkenylphosphoric acids obtained can in some cases be used as convenient phosphorylating reagents containing readily hydrolyzable vinyloxy groups.

Experimental Part

Quasiphosphonium compound from diisopropenyl phenyl phosphite and bromine. To a solution of 10 g (0.042 mole) of diisopropenyl phenyl phosphite in 20 ml of abs. benzene, with cooling and stirring, was added 6.7 g (0.042 mole) of a solution of bromine in 30 ml of abs. benzene. Formation of a light-yellow precipitate was observed; it became white when the reaction mixture was allowed to stand overnight in a refrigerator. The precipitate was separated, washed with ether and isopentane. Yield 15 g (90% of theoretical). A substance with a sharp odor; it darkens and melts in air. M.p. 38-40°.

Found, %: C 36.68; H 4.10; P 7.83
$C_{12}H_{15}O_3PBr_2$. Calculated, %: C 36.62; H 3.84; P 7.87

Bromanhydride of isopropenyl phenylphosphoric acid. To a solution of 41.8 g (0.18 mole) of diisopropenyl phenyl ester of phosphorous acid in 80 ml of abs. benzene, with ice cooling and stirring, was added dropwise 26.9 g (0.18 mole) of bromine dissolved in 60 ml of abs. benzene. After being kept in the cold for two hours, the reaction mixture was heated for one and a half hours at 70-80°. The white precipitate of the quasiphosphonium compound at first melted, and then decomposed completely. After removal of the solvent, the residue was distilled in vacuo. Obtained 44.9 g (90% of theoretical) of the bromanhydride of isopropenyl phenyl ester of phosphoric acid.

Evolution of methylacetylene upon decomposition of the quasiphosphonium compound. To 23.8 g (0.1 mole) of diisopropenyl phenyl phosphite in 60 ml of benzene, with cooling and stirring, was slowly added a solution of 15.8 g (0.1 mole) of bromine in 50 ml of abs. benzene. A white precipitate of the quasiphosphonium compound formed. The reaction mixture was heated on a water bath so that decomposition proceeded slowly. The gas evolved was trapped by two Drechsel bottles containing 32 g (0.2 mole) of bromine. After removal of the excess bromine with hyposulfite and distillation, 15.6 g (51% of theoretical) of 1,1,2,2-tetrabromopropane was obtained. B.p. 105°/9 mm, n_D^{20} 1.6175, d_4^{20} 2.6915, MR_D found 46.78, calculated 47.11. Literature data (^{4}): b.p. 105-107°/9 mm; n_D^{20} 1.6166, d_4^{20} 2.6870.

Bromanhydride of divinylphosphoric acid. To a solution of 23.7 g (0.13 mole) of butyl divinyl phosphite in 40 ml of abs. benzene, with ice cooling and stirring, was slowly added dropwise

19.9 g of bromine dissolved in 60 ml of absolute benzene. The mixture was then stirred for 1 hour at room temperature and then heated for one hour at 70-

90°. The benzene was distilled off, and the residue was distilled in vacuo. 20.2 g (80% of theory) of bromoanhydride of divinylphosphoric acid was obtained.

Chloroanhydride of diisopropenylphosphoric acid. To a solution of 20.2 g (0.09 mole) of *n*-butyl diisopropenylphosphite in 30 ml of dry carbon tetrachloride, while cooling with ice and stirring, 19.4 g (0.09 mole) of phosphorus pentachloride dissolved in 80 ml of dry carbon tetrachloride was added slowly, dropwise. The mixture was then heated for one hour at 70–80°. The carbon tetrachloride was distilled off, and the residue was distilled in vacuo. 12.4 g (70% of theory) of chloroanhydride of diisopropenylphosphoric acid was obtained.

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Note: Figure translations are in progress. See original paper for figures.